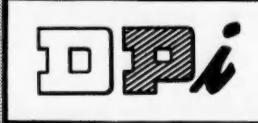


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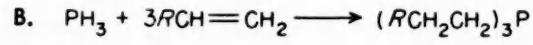
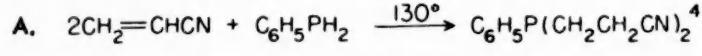
PREPARATION AND REACTIONS OF TERTIARY PHOSPHINES

By J. A. FORD JR.*

I. Preparation

The literature up to 1950 concerning methods of preparation of tertiary phosphines has been extensively surveyed (1). Of some fifteen synthetic routes that are mentioned, the most convenient one for laboratory use is the reaction of halogen derivatives of trivalent phosphorus with Grignard reagents (2) or organolithium compounds (3).

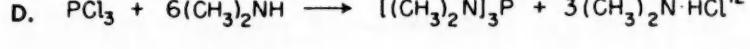
Since 1950 the most important preparative method to appear in the literature is the addition of trivalent phosphorus hydrides to carbon-carbon double bonds. The reaction conditions depend, of course, upon the nature of the olefins employed. In the case of activated double bonds, no catalyst is necessary. Otherwise, the use of catalysts, such as methanesulfonic acid (5), ultraviolet radiation (5), or di-tert.-butyl peroxide (6) is essential.



In place of phosphine, a mixture of white phosphorus and hydrogen can be heated with an olefin or diolefin at 250-400° C. under a pressure of 700-3000 atmospheres to produce tertiary phosphines (7).

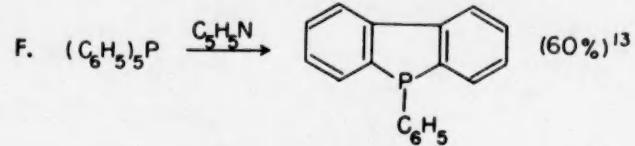
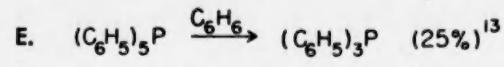
They may also be obtained from treatment of phosphorus with alkyl (8, 9) or silyl (10) halides.

A few other tertiary phosphines have recently been made which resemble the last one in not having three carbon-phosphorus bonds.



Decomposition of pentaphenylphosphorane has given tertiary phosphines.

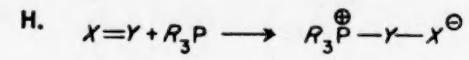
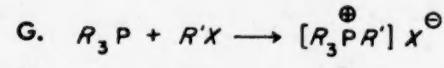
*Research Laboratories, Eastman Kodak Company, Rochester 4, New York.



Finally, reduction of tertiary phosphine oxides or sulfides with metal hydrides to the corresponding tertiary phosphine has been reported (14).

II. Reactions

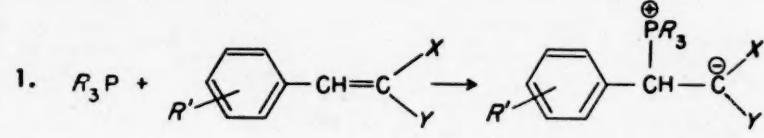
Tertiary phosphines are strong nucleophilic reagents and will form quaternary phosphonium salts either by reaction with alkyl halides or with compounds containing polarized or polarizable double bonds.



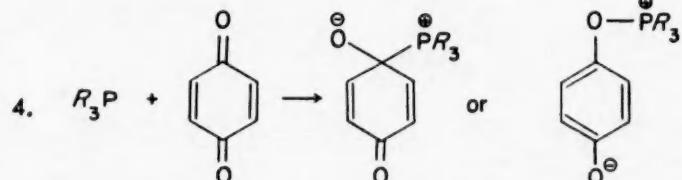
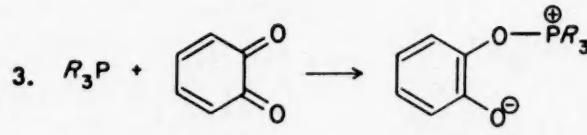
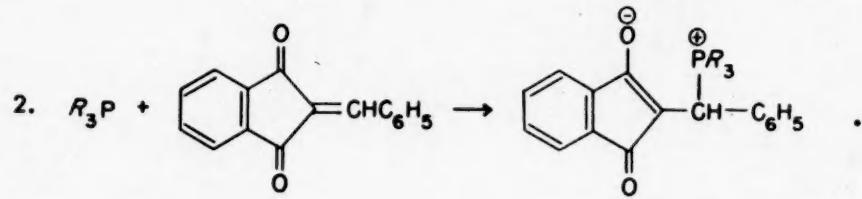
Formation of phosphonium salts with alkyl halides according to reaction (G) is usually done simply by heating them with the tertiary phosphine. Aromatic halides are more sluggish, but quaternization has been accomplished by treating the phosphine with an acetate-buffered aqueous solution of the aryl diazonium halide (15) or with a mixture of the aryl halide and a trace of cobalt chloride, followed by addition of phenyl magnesium bromide (16).

The unsaturated compounds undergoing reaction (H) may be divided into two groups: one in which X and Y are both carbon atoms and one in which X is a carbon atom and Y is an atom of another element.

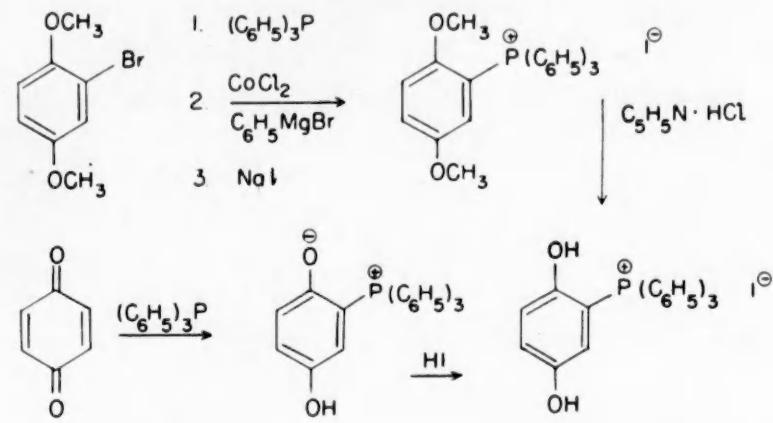
Examples of reaction (H) with the former group are (17):



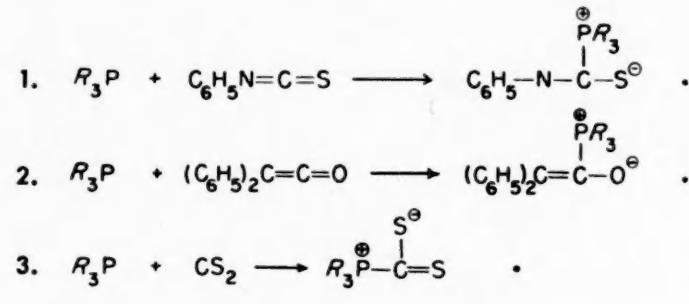
$X = Y = \text{CN}; \quad X = Y = \text{COOR}; \quad X = \text{CN}, \quad Y = \text{COOR}.$



Recently, it has been found that, while chloranil gives an adduct with triphenylphosphine corresponding to the second of the possible structures just given (18), the adduct from *p*-benzoquinone was different from either of them. The structure and the means of its elucidation are given here (19).

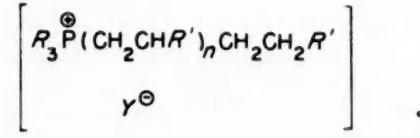
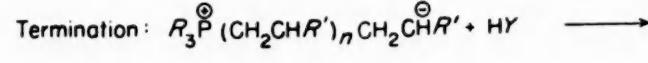
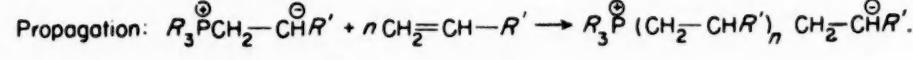
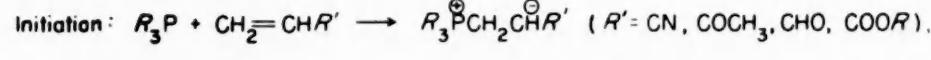


Examples of reaction (H) with the latter group (X and Y are not both carbon atoms) are (17):



The possibility has not been excluded that the tertiary phosphine-carbon disulfide adduct is a loose molecular compound without regular C-P or C-S bonds (20).

The anionic polymerization of electrophilically substituted olefins has been accomplished by the use of tertiary phosphines (17).



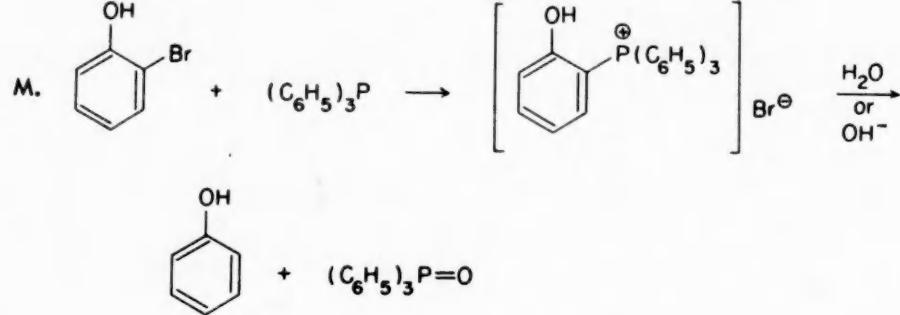
Tertiary phosphines are good reducing agents, the aliphatic members being much stronger than the aromatics in this respect.

yl-
8),
ure

- I. $2R_3P + O_2 \longrightarrow 2R_3P=O$
- J. $8R_3P + S_8 \longrightarrow 8R_3P=S$
- K. $R_3P + Se \longrightarrow R_3P=Se$
- L. $R_3P + X_2 \longrightarrow R_3PX_2$

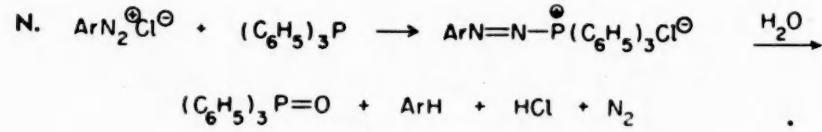
The reaction between sulfur and triarylphosphines has been studied kinetically (21). The reaction rate is strongly increased by ionizing solvents and by electron-releasing substituents in the aromatic ring. A mechanism is proposed which involves nucleophilic displacement of S_8 on S by the basic phosphine with S_8 ring opening to a dipolar ion that then reacts rapidly with more triarylphosphine.

Hydrogenolysis of *o*- or *p*-halophenols is accomplished by quaternizing them with triphenylphosphine and treating the quaternary salt with water or alkali (17).

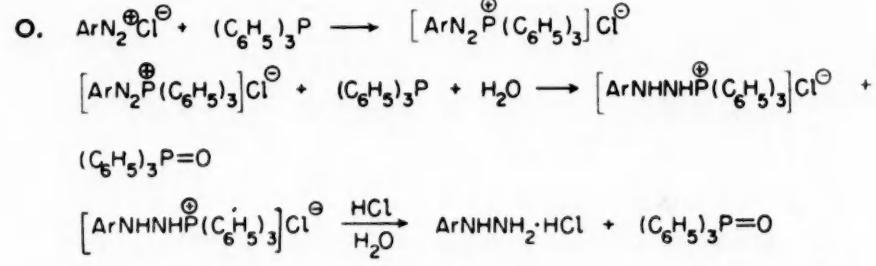


Peroxy compounds and many types of oxides are reduced by tertiary phosphines. Disulfides are reduced to sulfides (17).

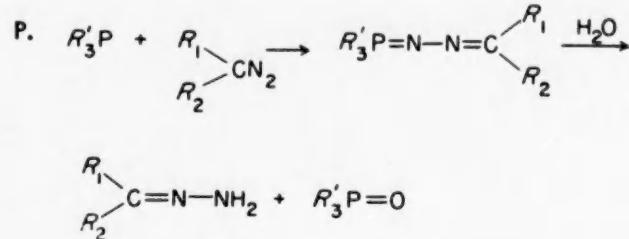
Along with quaternization which has already been mentioned, diazonium salts undergo some other reactions with tertiary phosphines (17). If equimolar amounts of the phosphine and diazonium salt are used, and the intermediate is subjected to aqueous hydrolysis, the following reaction occurs:



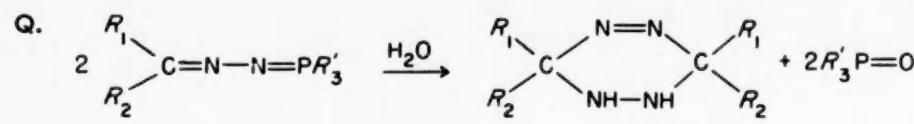
The use of two moles of triphenylphosphine per mole of diazonium salt, followed by quantitative acid hydrolysis causes this reaction sequence.



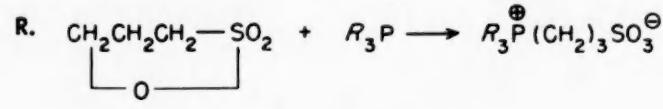
Diazoalkanes react with tertiary phosphines to form phosphazines which are hydrolyzed by water to hydrazones and phosphine oxides (17).



If only a small amount of water is used, a tetrazine is produced from the intermediate.



Tertiary phosphines react with sultones (22, 23) to give products which are useful as pesticides.



Several uses as catalysts have been found for tertiary phosphines (24-29). They may also act as catalyst poisons (30), although the toxicity may be destroyed by conversion to the phosphine oxide.

Finally, a reaction between triethylphosphine or triphenylphosphine and white phosphorus in the presence of ultraviolet radiation is reported to give red phosphorus and a by-product which, after nitric acid oxidation and treatment with lead ion, gives lead ethyl or *p*-nitrophenylphosphonate (31). It is concluded that red phosphorus is actually a polymeric compound having O and OH end-groups.

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